

PATENT SPECIFICATION

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(54) ELECTRO-CHEMICAL SYSTEMS

(71) We, UNION CARBIDE CORPORATION, a corporation organized and existing under the laws of the State of New York, United States of America, of 270 5 Park Avenue, New York, State of New York 10017, United States of America, (assignee of KARL VICTOR KORDESCH and AKIYA KOZAWA), do hereby declare the invention, for which we pray that a patent 10 may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to coherent manganese dioxide electrodes, a process for their production, and electrochemical cells utilizing them.

Particulate manganese dioxide mixed with powdered carbon and/or graphite is widely used as a cathode material or depolarizer in commercial batteries. It is relatively inexpensive and it provides a satisfactory power output. However, it has been the experience in the battery making art that manganese dioxide cathode mixes could not be compressed into bodies having sufficient cohesive strength to be self-supporting when they are wetted by electrolyte. Therefore, manganese dioxide electrodes have been provided with some sort of mechanical support or restraint when used in contact with liquid aqueous electrolytes. Such mechanical supports include metal containers surrounding annular electrodes, and compression on a stack of flat electrodes. Without such support, manganese dioxide electrodes will disintegrate fairly rapidly in liquid electrolyte, particularly alkali solutions. Disintegration will occur with time even when a fairly good cathode binder such as Portland cement (taught in U.S. Patent No. 2,962,540) is used. Mechanical support (e.g., a steel can surrounding the cathode) is still needed with cement binders. Cathode disinte-

gration becomes even more of a problem if the electrode is employed in a rechargeable cell where it is subjected to charge-discharge cycling. Lattice expansion on discharge and contraction on charge, a phenomenon peculiar to manganese dioxide, further adds to the problem of electrode disintegration.

Because manganese dioxide electrodes lacked the necessary cohesive strength when contacted by electrolyte, heretofore it has not been feasible to employ manganese dioxide as a depolarizer in the form of an unrestrained thin layer, which is the most effective form of efficient electrochemical utilization of the active material present. Because of the disadvantages mentioned above, manganese dioxide has been employed commercially as the depolarizer only in electrochemical cells delivering low and medium discharge currents, despite the fact that it has been demonstrated experimentally that manganese dioxide has high current capabilities.

By practice of the present invention one or more of the following advantages may be obtained:—

- (i) manganese dioxide electrodes having improved cohesion, especially when exposed to aqueous electrolytes;
- (ii) coherent, thin manganese dioxide electrodes;
- (iii) manganese dioxide electrodes capable of high discharge rates;
- (iv) a means for more efficient electrochemical utilization of manganese dioxide in electrochemical cells;
- (v) electrochemical cells having improved stability to changes in temperature;
- (vi) electrochemical cells having improved performance at low temperatures;
- (vii) manganese dioxide electrodes which have improved retention of properties on charge-discharge cycling.

The invention provides a coherent elec-

trode for use in an electrochemical cell having an aqueous electrolyte. The electrode is composed of particulate manganese dioxide, colloidal electrically conductive material, and particulate electrically conductive material, the said materials being bonded by an electrolyte-wettable polymeric binder. The colloidal electrically conductive material provides particle-to-particle electrical contact within the electrode. The electrode is characterized by resistance to swelling in aqueous electrolyte.

According to one aspect therefore the present invention provides a coherent electrode for an electro-chemical device having an aqueous electrolyte, which electrode is composed of (a) particulate manganese dioxide, (b) colloidal electrically conductive material, and (c) particulate electrically conductive material, said materials (a), (b) and (c) being bonded by an electrolyte-wettable polymeric binder, and said colloidal electrically conductive material providing particle-to-particle electrical contact within the electrode, the electrode being resistant to swelling in aqueous electrolyte.

In a further aspect the present invention provides a process for producing a coherent electrode for use in an electrochemical cell having an aqueous electrolyte, said process comprising:—

- (a) mixing (i) a polymeric binder, (ii) a colloidal electrically conductive material, (iii) particulate manganese dioxide, and (iv) particulate electrically conductive material, to produce a mixture; and
- (b) forming said mixture into a coherent electrode, in which the polymeric binder is of a nature such that said electrode is wettable by said electrolyte.

In yet a further aspect the present invention provides a electro-chemical device having an anode, a cathode, and an aqueous electrolyte in contact with said anode and cathode, in which in the charged condition said cathode is the electrode as defined immediately above.

The present invention will be described in detail hereinafter with reference to the accompanying drawings, in which:—

Fig. 1 is a perspective view of a flat manganese dioxide electrode embodying the principles of the invention;

Fig. 2 is an exploded perspective view of the elements of a cell embodying the principles of the invention, in unassembled condition;

Fig. 3 is a side sectional view of an assembled cell of the type shown in Fig. 2;

Fig. 4 is an exploded view of another type of cell embodying the principles of the invention;

Fig. 5 is a graph of rate of discharge versus per cent utilization of manganese dioxide and total capacity in a Zn/KOH/MnO₂ cell of the invention compared with a Zn/KOH/MnO₂ cell of the prior art;

Fig. 6 is a graph of discharge time versus voltage for both freshly made Zn/KOH/MnO₂ flat cells of the invention and such cells after storage for one month at 125°F., and compares their performance with the performance of a commercial Zn/KOH/MnO₂ cell;

Fig. 7 is a graph of discharge time versus voltage for Zn/KOH/MnO₂ flat cells of the invention and of commercial Zn/KOH/MnO₂ cells, at room temperature, at 0°C., and at -12°C.;

Fig. 8 is a graph showing the charge/discharge cycle performance of a rechargeable Cd/KOH/MnO₂ flat cell constructed in accordance with the principles of the invention;

Figs. 9 and 10 are graphs showing the charge-discharge cycle performance of rechargeable Zn/KOH/MnO₂ flat cells constructed in accordance with the principles of the invention;

Fig. 11 is a graph showing discharge time versus voltage of Zn/KOH/MnO₂ cells of the invention at various current densities;

Figs. 12 and 13 are graphs showing discharge time versus voltage of, respectively, Mg/MgBr₂/MnO₂ and Pb/H₂SO₄/MnO₂ wet cells of the invention;

Fig. 14 is a graph of high current drain pulsing performance of a Zn/KOH/MnO₂ cell of the invention;

Fig. 15 is a perspective, partially schematic view of a unit cell embodying the principles of the invention, the electrodes being connected in parallel;

Fig. 16 is a schematic perspective view of a battery case designed to contain eight unit cells of the type shown in Fig. 15, connected in series;

Fig. 17 is a graph showing the discharge time versus voltage of a unit cell of the type shown in Fig. 15 and a commercial lead/acid cell;

Fig. 18 is a graph showing the high current drain pulsing performance of a unit cell of the type shown in Fig. 15; and

Fig. 19 is an enlarged, idealized cross-sectional view of a portion of a manganese dioxide electrode embodying the principles of the invention.

Referring first to the drawings, Fig. 1 shows a thin, flat manganese dioxide electrode 21 embodying the principles of the invention, and having a metal screen current collector 22 embedded therein. The method for fabricating the electrode will be described in detail hereinafter. Figs. 2 and 3 show a flat cell utilizing a manganese dioxide electrode 21 of the type shown in Fig. 1. The cell includes a manganese dioxide electrode 21 disposed between two zinc screens 23 and 24, the manganese dioxide electrode 21

and the zinc screens 23 and 24 being separated by suitable separators 25 and 26, such as fibrous-reinforced regenerated cellulose. A suitable electrolyte is absorbed in the separators 25 and 26. The cell is contained in a case 27 made of a suitable plastic material such as polystyrene. In the charged condition, the manganese dioxide electrode 21 is the cathode, and the zinc screens 23 and 24 comprise the anode.

The principle of alternating flat anode and flat cathode separated by suitable separators and encased in a plastic case, as shown in Figs. 2 and 3, can be employed to fabricate flat cells composed of at least two flat manganese dioxide electrodes and at least two flat metal electrodes, with the electrodes normally being connected in parallel.

In Fig. 4, one type of round cell utilizing the manganese dioxide electrodes of the invention is shown. The cell comprises, in the charged condition, a rolled manganese dioxide cathode 28 coated on a suitable wire screen current collector 29, and a zinc foil anode 31, the two electrodes being separated by a suitable separator such as one or two layers of modacrylic fibers 32 and 33. The rolled up electrodes are contained in a cylindrical steel can container 34. A suitable electrolyte is absorbed in the separators 32, 33.

In Fig. 15, a unit cell is shown that is fabricated from a plurality of alternating flat manganese dioxide cathodes and pressed powdered zinc anodes, with the electrodes being connected in parallel and separated by suitable separators. The unit cell is contained in a plastic case 35, with the cathode current collector 36, the anode current collector 37, and a filling port 38 extending out of the top of the case 35.

Fig. 16 shows a battery case 39 that is designed to contain eight unit cells of the type shown in Fig. 15, connected in series. Each of said unit cells is contained in one of the compartments described by the partitions 41.

Fig. 19 shows an enlarged, cross-sectional view of a portion of a representative manganese dioxide electrode of the invention. As this drawing illustrates, particles of manganese dioxide 42 and acetylene black 43 (as the particulate electrically conductive material) are embedded in a porous matrix of a polymeric binder 44. The polymeric binder 44 contains colloidal graphite to render it conductive. The binder/colloidal graphite matrix serves two purposes: first, to mechanically bind the particles of manganese dioxide 42 and acetylene black 43 to render the electrode resistant to swelling when it is contacted by aqueous electrolyte; and second to provide interparticle electrical contact within the electrode.

The manganese dioxide electrodes of the

invention can be produced by a process which comprises:

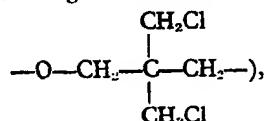
mixing a polymeric binder, a colloidal electrically conductive material, particulate manganese dioxide, and particulate electrically conductive material, to produce a mixture; and

forming said mixture into a coherent electrode.

To briefly illustrate one mode of carrying out this process, two grams of an epoxy resin (the diglycidyl diether of bisphenol A) plus amine hardener mixture is dissolved in 14 grams of an alcoholic (isopropyl alcohol) suspension of colloidal graphite. A mixture containing 90 weight per cent particulate manganese dioxide and 10 weight per cent particulate electrically conductive material (8 per cent graphite powder plus 2 per cent acetylene black) is then mixed with the epoxy/colloidal graphite mixture in the ratio of 30 grams of the manganese dioxide mixture to 12 grams of the epoxy/colloidal graphite mixture. The mixture has a putty-like consistency, which makes it easy to spread on a metal screen current collector. Pressure may be used, if desired, to fill the holes in the screen for uniformly and to insure good contact between the mixture and the collector. The mixture on the screen support is then heated for about one half hour at about 50°C. in order to drive off the liquids present in the mixture and to harden the epoxy resin. The coherent electrode is then ready to be incorporated in conventional manner as an electrode in an electrochemical cell.

The polymeric binder that is employed in the invention is one that, in its ultimate form in the finished electrode, will permit the electrode to be wetted by the electrolyte to be used in the cell, but at the same time, the electrode will be resistant to swelling by the electrolyte, which is the cause of weakness in prior art manganese dioxide electrodes. The term "wetted" refers to a surface condition in which the electrolyte is permitted to penetrate the pores of the electrode to achieve maximum ionic contact between the electrolyte and the active material in the electrode.

In addition to epoxy resins as exemplified above, the polymeric binder can be a polymer such as an acrylonitrile-butadiene-styrene (ABS) polymer, an acrylate polymer such as polymethyl methacrylate or other polymer of a lower alkyl (e.g., C₁ to C₄ alkyl) ester of acrylic or methacrylic acid, a melamine- or urea-formaldehyde polymer, a chlorinated polyether (e.g., a polymer having the recurring structural unit



a polycarbonate, a phenol-formaldehyde polymer, a polysulfone, polystyrene and styrene copolymer with monomers such as acrylonitrile, a vinyl resin such as polyvinyl chloride, polyvinyl alcohol, or vinyl chloride-vinyl acetate copolymer, and a styrene-butadiene copolymer.

The polymeric binder can contain conventional additives such as stabilizers and plasticizers which are substantially inert in the electrochemical cell environment.

The binder selected should be stable in the electrolyte to be used in the cell in which the electrode will be employed. Thus, for instance, polyvinyl alcohol, ABS resins, urea/formaldehyde resins, and phenol/formaldehyde resins should not be employed in alkaline cells since they are not stable to alkali over extended periods of time. The stability of the polymeric binder toward the electrolyte is either known or readily determined by the worker in the art. Binders which are stable in alkaline electrolyte include polysulfone, acrylic polymers such as polymethyl methacrylate, epoxy resins, and polystyrene.

In forming the electrode mixture, it is preferred that the polymeric binder be in a liquid vehicle in order to facilitate thorough mixing of the ingredients of the electrode mix. Thus, it is desirable to employ the binder in solution, since most of the polymers are normally solid materials. Even in the case of epoxy resins, which are liquids prior to the hardening reaction, it is preferred to employ a solution because most epoxy resins are rather viscous at room temperature, and a solution of an epoxy resin is more readily mixed to form a uniform mixture than is the undiluted, viscous resin. As another alternative, the polymeric binder can be employed in the form of a powder, which can be dispersed in a liquid, if desired.

The liquid that is employed as a solvent or dispersant for the polymeric binder will depend somewhat on the nature of the polymeric binder. In addition to being either a solvent or a dispersant for the polymeric binder, the liquid should also be inert towards the electrode mix. For instance, the liquid should preferably not be readily oxidized by the manganese dioxide in the mix. Examples of such useful liquids include organic liquids such as isopropyl alcohol, tert-butyl alcohol, hexyl alcohol, and other alcohols. Other useful liquids include ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone. Chlorinated hydrocarbons such as methylene dichloride, chloroform, trichloroethylene, perchloroethylene, and other solvents such as tetrahydrofuran are also useful in the invention. In many cases, it is useful to employ a mixture of liquids. The liquid employed must be volatile. As used herein, the term "volatile" means that the liquid is

capable of substantially complete volatilization at moderate temperatures, for instance, at temperatures of up to 100°C.

Another component that is employed in the process of the invention is a colloidal electrically conductive material. Such electrically conductive materials include graphite, carbon black, and metal powders such as silver and nickel powder. The colloidal electrically conductive material is preferably employed as a colloidal dispersion in a liquid. As is known in the art, the individual particles of the colloidal electrically conductive material are mostly of submicron size. The liquids that can be used as the dispersant for the colloidal electrically conductive material includes those that were mentioned above as solvents or dispersants for the polymeric binder. Colloidal graphite is the preferred colloidal electrically conductive material, and it is preferably employed as a colloidal dispersion in a chlorinated hydrocarbon such as trichloroethylene or in an alcohol such as isopropyl alcohol.

The third principal component of the electrodes of the invention is particulate manganese dioxide. The known forms of particulate manganese dioxide customarily used in batteries can be employed in the invention. Such forms include natural ore (e.g., pyrolusite), chemically treated natural ore, electrolyte manganese dioxide, and chemically prepared manganese dioxide.

Particulate electrically conductive material is also employed in the manganese dioxide electrodes. Known materials that are customarily employed in manganese dioxide depolarizer mixes can be used. These include acetylene block and powdered graphite.

In the electrodes of the invention, the manganese dioxide is the electrochemically active material. The polymeric binder provides cohesive strength to the electrode and permits the electrode to be wetted by electrolyte. The particulate electrically conductive material serves a purpose analogous to a principal purpose of the acetylene black or powdered graphite in the known manganese dioxide depolarizer mixes. That purpose is to improve the electrical conductivity of the electrode. The colloidal electrically conductive material is employed to overcome a problem associated with the use of the polymeric binder in the electrode. The binder tends to coat the particles of manganese dioxide and particulate electrically conductive material. Since the polymers that are employed as binders are non-conductors of electricity, in the absence of the colloidal electrically conductive material, the binder would tend to form an insulative coating around the individual particles of both the manganese dioxide and the particulate electrically conductive material. The colloidal material overcomes this tendency and ensures

particle-to-particle electrical contact within the electrode. Stated another way, the colloidal material, when mixed with the polymer, causes the binder to be conductive rather than insulative.

As a general rule, the colloidal electrically conductive material, the polymeric binder, and the particulate electrically conductive material, are all preferably used in the minimum amounts that can be employed and still effect the above-mentioned purposes. This is because it is desirable to have as large a proportion of manganese dioxide in the electrode as possible in order to provide the maximum service in ampere-hours capacity per unit weight of cell.

As a general rule, the minimum amounts of components that can be used and still effect the desired purposes are the following:

Colloidal electrically conductive material—about 1 to 2 weight per cent
 Particulate electrical conductive material—about 5 to 10 weight per cent
 Polymeric binder—about 1 to 2 weight per cent

The remainder of the electrode is manganese dioxide. (Percentages are based on weight of finished electrode, not including the current collector). As can be seen from the above percentages, manganese dioxide can constitute at least 85 or 90 weight per cent of the electrode mix, and will normally constitute at least about 70 weight per cent of the electrode mix. Manganese dioxide electrode mixes in commercial use today generally contain a maximum of about 70—80 weight per cent manganese dioxide.

The above described ingredients are employed in making cohesive manganese dioxide electrodes. The components are first thoroughly mixed together to form a mixture. It is preferred to first mix the polymeric binder and the colloidal electrically conductive material, and then add the remaining components. This helps to ensure that optimum electrically conductive contact will be made between the colloidal electrically conductive material and the particles of manganese dioxide and particulate electrically conductive material with a minimum of time being expended in the mixing operation.

The type of mixing employed in making the mixture is not critical. Simple stirring until the ingredients are substantially uniformly mixed will be sufficient in most cases.

The mixture is then formed into an electrode. In most cases, it is desirable to form the electrode by coating a current collector such as a metal or carbon screen or fabric with the mixture, which will normally be in the form of a relatively thick paste. Conventional coating or spreading techniques can be employed. In one desirable aspect of the invention, the electrode is formed by forming a laminate or sandwich of two current col-

lector screens or fabrics having the mixture between them. This helps to eliminate problems that may occur from gassing if the cell is overcharged. Pressure is desirable in many cases in order to improve the contact between the mixture and the current collector. If desired, the current collector can be coated with a material such as a lubricating graphite, sintered metal powder, or electroplated silver in order to improve the electrical contact between the electrode mixture and the current collector screen. The current collector can be made from any suitable material that is inert in the system. Steel, nickel, carbon, silver, and nickel- or silver-coated steel are examples of current collectors that can be employed.

The liquids that are present in the electrode mix are removed after the electrode has been shaped or given its final form. They can be removed from the mixture simply by air drying, although in many cases moderate heating is desirable. Moderate heating is also desirable for effecting a hardening reaction if the polymeric binder is a thermosetting resin such as an epoxy resin system. While epoxy resins often can harden at room temperature, the hardening is considerably speeded up by heating. One-half to about one hour at about 40° to 50°C. can be used as the heating step.

In order to improve the contact of the electrode mixture with the current collector, and to eliminate bubbles from the mixture, the electrode can be pressed in a press prior to the drying step. Pressures of from a few hundred to several thousand psi are suitable.

Before the liquids have been completely removed from the mixture, and before any hardenable resins have been cured, the electrodes of the invention can be shaped into many different physical shapes. For instance, they can be rolled up into a spiral, they can be bent, or they can be simply produced in the form of flat electrodes.

One of the important aspects of this invention is that the coherent manganese dioxide electrodes can be made in the form of thin layers. Thus, manganese dioxide electrodes having thicknesses of from about 10 to about 50 mils can be fabricated employing the principles of the invention. The importance of this aspect of the invention resides in the fact that thin electrodes provide a means for efficient electrochemical utilization of the active material present, and for the fabrication of cells delivering unusually high rates of discharge with relatively efficient utilization of the manganese dioxide. All of the electrodes of the invention, thin or otherwise, can be employed in rechargeable cells having prolonged cycle life.

The electrodes of the invention are porous. The porosity is such that the electrode will absorb from about 20 to about 40 weight percent (based on weight of electrode) of

electrolyte. The porosity is achieved, in most cases, by the evaporation of the liquid used in formulating the mix. If no volatile liquids are used in formulating the electrode mix, then porosity is achieved by other means known to the art, such as by including in the mix a compound that can be decomposed to gaseous components at low temperatures. Ammonium carbonate is an example of such a compound.

The manganese dioxide electrodes of the invention are incorporated in electrochemical cells by known procedures. The electrodes can be employed as cathodes with known types of anodes such as zinc, magnesium, cadmium, aluminum, and lead anodes. Either aqueous alkaline or aqueous acid electrolytes can be employed, depending on the type of cell desired and, in some cases, the nature of the anode.

In the Examples, the generalized procedure set forth below as Method 1 was employed, unless otherwise indicated.

Method 1

25 Current Collector

A 5-mil thick, annealed, nickel plated steel screen is employed as the current collector. In order to improve the adhesion of the electrode mix to the screen, it is desirable to employ a primer. The primer contains conductive material such as colloidal graphite and a polymer that will be softened by the solvent contained in the electrode mix. The following formulations are useful as primers for electrode mixes containing polymethyl methacrylate and polysulfone, respectively:

Primer 1:

5 grams polymethyl methacrylate
100 milliliters solvent (trichloroethylene,
chloroform, dichloromethane or mixtures thereof)
300 grams colloidal graphite suspension containing 10 weight per cent graphite in trichloroethylene

45 Primer 2:

10 grams polysulfone (PRDA-8030, Union Carbide Corporation)
100 milliliters dichloromethane
300 grams colloidal graphite suspension

50 (The colloidal graphite that is employed in the Examples, unless otherwise indicated, is a commercial product marketed under the trade name "DAG No. 155", by the Acheson Colloids Division of Acheson Industries, Inc., Port Huron, Michigan).

55 In addition to the use of a primer to improve adhesion to the screen, high current performance of the electrode is improved by silver plating the nickel-plated screen prior to priming. Only a very thin coating of silver (a silver "strike") is used.

Manganese Dioxide Formulation

Electrolytic manganese dioxide is employed. The particulate electrically conductive material employed is powdered graphite having a particle size such that it passes through a screen having 200 meshes per inch (U.S. Standard Sieve Series). It is a commercial product marketed under the trade name "Dixon Air-Spun Graphite, Type 200-09", by the Joseph Dixon Crucible Company, Jersey City, New Jersey. In some cases, modacrylic fibers or carbon fibers are added to the electrode mix to improve cohesion. In cases where the electrode mixture needs to have improved conductivity and/or hydrogen absorption properties, Ag_2O is added. The following manganese dioxide formulation is useful:

Manganese Dioxide Formulation:

1000 grams electrolytic manganese dioxide	65
100 grams Powdered graphite	
20 grams modacrylic fibers, 1/8-inch long (optional)	70
10 grams Ag_2O (optional)	75

Binder Formulations

The polymeric binder formulations employed were the following:

Polysulfone Formulation: 90

10 grams 10 weight per cent polysulfone solution in dichloromethane and/or trichloroethylene	90
10 grams colloidal graphite suspension, 10 weight per cent in trichloroethylene	95

(This formulation is preferably prepared on the day it is used).

Polymethyl Methacrylate Formulation:

10 grams of 5 weight percent polymethyl methacrylate solution in chloroform, dichloromethane, and/or trichloroethylene	100
10 grams of 10 weight per cent colloidal graphite suspension in trichloroethylene	105

(This formulation preferably is prepared just prior to its intended use, e.g., within about one-half hour).

Electrode Mixes

The following formulations are typical of the electrode mixes employed in the Examples:

Polysulfone spreadable mix: 110

30 grams manganese dioxide formulation	110
18 grams polysulfone formulation	

Polymethyl methacrylate spreadable mix: 115

30 grams manganese dioxide formulation	115
18 grams polymethyl methacrylate formulation	

After the spreadable mix is spread onto the primed screen, the electrode is placed between plates using absorbent paper as an intermediate layer between the electrode and the plates. The electrode is pressed at 5000 psi for one minute, and the pressure is then raised to 10,000 psi for one minute. The electrode is then dried in open air to remove the volatile solvents. If the organic liquid used is all or predominantly trichloroethylene, heating for about one hour at 40°C. is desirable to remove all of the liquid. 65

If the electrode is to be shaped, for instance by rolling into a spiral configuration, this shaping is done after the pressing but before the drying. 70

The dried plates have a thickness of 25 to 30 mils when the spreadable mix is applied in a thickness of 100 mils. The dried plates have a weight of about 1.5 grams/square inch (including the single metal screen current collector, which weighs 0.2 grams/square inch). 75

The polysulfone-containing electrode described above contains about 80 to 85 weight per cent manganese dioxide, about 9 to 10 weight per cent powdered graphite, about 2.5 to 3 per cent polysulfone, and about 2.5 to 3 per cent colloidal graphite. The polymethyl methacrylate-containing electrode contains about 82 to 87 weight per cent manganese dioxide, about 9 to 10 per cent powdered graphite, about 1.2 to 1.5 per cent polymethyl methacrylate, and about 2 to 3 per cent colloidal graphite. 80

Method 2

The following is an alternate procedure for producing the cohesive manganese dioxide electrodes of the invention:

1. Conductive Polymeric Binder: 100 grams of a 10 weight per cent polysulfone solution (using 60 per cent trichloroethylene and 30 per cent chloroform as solvents) is mixed with 100 grams of 10 weight per cent colloidal graphite suspension in trichloroethylene. 85
2. Conductive Polymeric Binder Plus Powdered Graphite: Mix 200 grams of powdered graphite with enough trichloroethylene to obtain a paste; then add 200 grams of conductive polymeric binder and mix well. Place in a well-ventilated oven at 70°C. and allow mixture to dry. Remove the mixture from the oven and grind to a powder. 90
3. Partially and conductively bonded graphite plus manganese dioxide: Mix 150 grams of the powder obtained in the step immediately above with 850 grams of electrolytic manganese dioxide. The said powder and manganese dioxide must be thoroughly mixed. 95
4. Rebonding (tacking) of mix: Spray into mixture obtained from step 3 (while mixing) a fine spray of trichloroethylene until mix is damp. Then without allowing mix to dry, prepare molded cathodes, using 600 psi pressure, by procedures analogous to those described above in Method 1. 100

5. Solvent Removal: Place cathodes in well-ventilated oven for 15 minutes at 50°C. to dry. (This procedure can be used only when a normally solid binder is used that can be re-softened or re-dissolved by the addition of a small amount of solvent in the 4th step). 105

Example 1

One of the advantages that can be obtained by practicing the invention is the preparation of thin electrodes which are very efficient in their utilization of the manganese dioxide in the electrode. This example illustrates the efficient utilization of the manganese dioxide in a thin electrode constructed in accordance with the invention.

A flat cell was constructed similar to the one shown in Figs. 2 and 3, and having two 5 mil thick expanding zinc anodes and one manganese dioxide cathode constructed as set forth above (Method 1) using polymethyl methacrylate as the binder. (Silver oxide was omitted from the manganese dioxide formulation). The cathode was 25 mils thick, was about 1.5 square inches in area (about 10 square cm), and contained about 2.0 grams of the cathode mix (80 weight per cent manganese dioxide). The electrolyte was 9 N aqueous KOH. 110

The cell described above and many others similarly constructed, which had initial closed circuit voltages of about 1.4 volts, were discharged at various constant current rates until the voltage dropped to 1.0 volt. 115

The discharge time of these cells was plotted against cell voltage at various constant discharge current densities and compared on the basis of milliamperes per gram of manganese dioxide, as shown in Fig. 11. As a specific illustration, a thin manganese dioxide cathode containing 1.6 grams of manganese dioxide (80 per cent of 2 grams of mix) delivers about 2.2 hours of service at 0.1 ampere (62.5 mA per gram of manganese dioxide) constant current to a 1.0-volt cutoff, corresponding to 0.22 ampere-hour (see 100 mA curve in Fig. 11). Theoretically, this electrode should have delivered 0.496 ampere-hours service. (0.496=1.6×0.31—Assuming that the cell reaction involves conversion of MnO₂ to Mn₂O₃ on discharge of a cell, and that such conversion is complete, one gram of manganese dioxide yields about 0.31 ampere-hour of electricity). The efficiency of manganese dioxide utilization in this electrode (to 1.0-volt cutoff) is therefore about 45 per cent. 120

Figure 5 compares the average efficiencies of thin manganese dioxide cathodes of this invention contained in flat cells of the type 125

described above, with the average efficiencies (in utilizing manganese dioxide) of commercial D-size alkaline round cells, each of the latter having 35 grams of manganese dioxide 5 in the cathode shell molded inside the steel container. The current drain for cells containing this type of manganese dioxide cathode corresponding to a drain of 62.5 mA/gram manganese dioxide would be 2.2 amperes ($35 \times .0625$). According to experimental testing, this cell averages such service (i.e., constant current drain of 2.2 amperes) for 0.7 hour, corresponding to 1.54 ampere-hours. The theoretical value would be 10 $35 \times 0.31 = 10.85$ ampere-hours. The average efficiency of utilization of manganese dioxide in this cell is thus about 14 per cent. The cutoff voltage used in this comparative test was 0.7 volt for the commercial cell 15 (at 2.2 amperes), since the voltage drop owing to its internal resistance is higher than that of the thin, flat cathode of this invention. The 1.0-volt cutoff was still used for the thin cathode of the invention. It should be further noted in Fig. 5 that at still higher rates of discharge, the average efficiency of manganese dioxide utilization in the commercial cell dropped off drastically compared to that observed with the thin electrodes of this invention.

This Example demonstrated the extraordinary efficiency in utilizing the electrochemical energy of manganese dioxide that is a feature of the thin electrodes of the invention. Thus, the thin manganese dioxide electrodes of the invention are capable of utilizing at least 25 per cent, and in many cases at least 35 per cent, of the electrochemical energy of manganese dioxide at a constant rate of discharge of 100 mA (milliamperes) 20 per gram of manganese dioxide vs. a zinc reference electrode using 9 N aqueous KOH as the electrolyte, before the voltage drops under about 0.9 volt. The electrochemical energy of manganese dioxide as used herein refers to the theoretical amount of electricity, in ampere-hours, that would be obtained upon complete conversion of MnO_2 to Mn_2O_3 on discharge of the cell.

Example 2

The electrodes constructed in accordance with the principles of the invention are relatively stable to extremes of temperature, both hot and cold. This example illustrates this advantage.

In this Example, flat cells having alternating flat anodes and cathodes (as illustrated in Figs. 2 and 3) connected in parallel were employed. These flat cells each contained three thin, flat manganese dioxide cathodes prepared as described above (Method 1). Each cathode contained 2 grams of cathode mix (about 1.6 grams of manganese dioxide), and each was about 1.5 inches in area. The four anodes were zinc, the electrolyte was 9 M aqueous KOH, and the separators were fibrous reinforced regenerated cellulose.

The performance of the flat cells after storage at high temperature (125°F., or about 50°C.), and at low temperatures (0°C. and -12°C.) was evaluated and compared with the performance of commercial AA size MnO_2/zinc alkaline cells, which are comparable in volume to the flat cells of this Example. The cells of the invention weighed 16-19 grams each, compared with 24 grams each for the commercial AA cells, including the steel cans. The flat cells each contained about 6 grams of manganese dioxide, and the AA cells each contained about 7 grams of manganese dioxide.

The flat cells and the commercial AA cells were discharged at a constant current of 350 mA at room temperature, both as produced and after storage of 125°F. for one month. The results of these tests are shown in Fig. 6, in which voltage against time is plotted. After storage for one month at 125°F., the flat cell of the invention retained a significantly higher proportion of the original performance than did the commercial AA alkaline cell.

The flat cells of the invention and the commercial AA cells were discharged at a constant current of 220 mA at room temperature, at 0°C., and at -12°C., and the voltage against time was plotted. The results are displayed in Fig. 7. The low temperature performance of the flat cell of this invention is significantly better than that of the commercial AA cell, despite similar room temperature performance.

Example 3

The cells of the invention can be employed as secondary or rechargeable cells. The following two experiments illustrate the rechargeability of the cells of the invention:

A. $\text{MnO}_2/\text{KOH}/\text{Cd}$ Cell.

A flat cell having alternating anodes and cathodes (as illustrated in Figs. 2 and 3) connected in parallel was fabricated from two thin manganese dioxide cathodes made in accordance with the description above (Method 1), three commercial cadmium anodes, and 9 M aqueous KOH as the electrolyte. The cathodes each weighed 2.2 grams (about 1.6 grams manganese dioxide) and were 1.5 square inches in area. The cell was discharged and charged at a constant current of 0.2 ampere over a number of cycles, with charge beginning when the cell was discharged to 0.8 volt and continuing until 1.5 volts was reached. The cathode current density was 10 mA/cm² and the rate of discharge was 50 mA/gm of cathode mix. Figure 8 shows the cycling performance through the 100th cycle.

At the voltage settings employed, during the first 40 cycles the cell reached a depth of discharge of about 75 per cent. As the cycling continued, the level of discharge decreased to about 50 per cent.

The cell delivered a total of 180 cycles, but beyond 130 cycles the internal resistance increased and the charge acceptance decreased below practical levels.

10 B. $\text{MnO}_2/\text{KOH}/\text{Zn}$ Cell.

A cell was fabricated from a thin manganese dioxide cathode as shown in Fig. 1, and made by the procedure described above (Method 1), a gelled zinc powder anode, and 15 9 M aqueous KOH electrolyte. The cathode weighed 2 grams (about 1.6 grams manganese dioxide), and was 1 square inch in area. The electrodes were separated by two layers of regenerated cellulose. Discharge and 20 charge time for the cell was 1 hour at 0.1 ampere constant current.

Fig. 9 displays the charge-discharge cycling performance of this cell through 58 cycles at a constant current density of 50 mA/gram of manganese dioxide (the charge 25 and discharge current was 0.1 ampere). The useful life of this cell was about 55 cycles under the conditions tested. The cathode then exhibited low charge acceptance and zinc 30 dendrite formation occurred.

When a lower rate of discharge, for instance 25 mA/gram of manganese dioxide, many more cycles can be obtained. For instance, Fig. 10 shows the cycling performance of a cell similar to the one described above, but which had two thin manganese dioxide cathodes connected in parallel instead of one. (The anode was between the cathodes, in a manner analogous to that shown in Figs. 2 and 3). The charge and discharge currents were the same, 0.1 ampere. A rate of discharge of 25 mA/gram of manganese dioxide in the cathode mix would correspond to a current of about 1.0 ampere in a D-size cell. 45 The maximum recommended discharge current for a typical commercial D-sized rechargeable $\text{MnO}_2/\text{KOH}/\text{Zn}$ cell is 0.625 ampere. This comparison provides an illustration of the high performance capabilities 50 of the cells of the invention.

This Example illustrated the long cycle life that can be obtained with rechargeable cells utilizing the manganese dioxide electrodes of the invention. As a general rule, rechargeable cells utilizing the manganese dioxide electrodes of this invention will be able to undergo at least 150 charge-discharge cycles when discharged to 30 per cent of full discharge at a constant rate of discharge of 60 100 mA per gram of manganese dioxide, before cathode failure occurs. Cathode failure will take the form of poor charge acceptance, increase in resistance, or the like.

**Example 4
Flat Rolled-Up ("Jelly Roll") Alkaline MnO_2/Zn Cell**

A C-size primary alkaline-zinc round cell (of the type shown in Fig. 4) was fabricated using a zinc foil anode, a modacrylic fiber separator, and a polymethyl methacrylate-bonded manganese dioxide cathode coated and pressed on a screen (Method 1), rolled up in a spiral ("jelly roll"), and inserted in a steel container. The electrolyte was 9 N KOH containing 1 per cent by weight ZnO . The binder concentration in the cathode mix was 2 per cent by weight. Cathode dimensions were 8 inches in length by 1-1/4 inches in width by 0.020 inch thickness. Anode dimensions were comparable.

In comparison with a D-size commercial alkaline cell, the smaller C-size cell of this invention showed superior discharge performance in that it was capable of supporting 4 amperes constant current for nearly 1 hour while the commercial cell failed within 10 minutes on the same drain, (in both cases, 1.5 volts was the initial voltage and 0.8 volts the cutoff voltage).

A rolled-cathode manganese dioxide-zinc cell of this type is comparable in power output to the same size Ni-Cd cell having a rolled, sintered nickel oxide cathode. The manganese dioxide cell actually surpasses the Ni-Cd cell in initial capacity and performs far better after storage at elevated temperatures.

This and other Examples demonstrate the high rate of discharge capability that is a feature of cells utilizing the thin manganese dioxide electrodes of the invention. Thus, the thin electrodes of the invention are capable of discharging above about 0.9 volt at a constant current rate of at least 250 mA per gram of manganese dioxide vs. a zinc reference electrode using 9 N aqueous KOH as the electrolyte. At this high discharge rate, the thin manganese dioxide electrodes of the invention are capable of utilizing at least about 15, and in some cases at least about 20, per cent of the electrochemical energy of the manganese dioxide contained in the electrode.

**Example 5
 $\text{Mg}/\text{MgBr}_2/\text{MnO}_2$ Cell
(90% MnO_2 in Mix)**

A $\text{Mg}/\text{MgBr}_2/\text{MnO}_2$ wet cell was made up using a Mg plate anode, aqueous 4 N MgBr_2 electrolyte, and two thin manganese dioxide cathodes (of the type shown in Fig. 1) made with the Ag_2O -containing formulation described above in Method 1, except that 60 grams of powdered graphite was used instead of 100 grams. Polymethyl methacrylate was the binder. Discharge performance on a 0.5-ampere continuous drain is shown in Fig. 12.

Example 6 Pb/H₂SO₄/MnO₂ Cell

A wet cell of this invention was assembled with 20 weight per cent aqueous H_2SO_4 as electrolyte, a lead anode from a commercial lead-acid battery, and two thin manganese dioxide cathodes (Fig. 1) of the same mix composition described in Example 5, except that a polysulfone binder was substituted.

Example 7

High Current Drain Performance

The behaviour of thin bonded MnO₂ cathodes at extremely high current outputs was studied in a four ampere-hour, box-type cell (Fig. 15) in pulse tests (described below) simulating the cranking of an engine.

This cell contained 6 thin manganese dioxide cathodes and 7 gelled zinc powder anodes connected in parallel, each electrode measuring 2 inches \times 2-1/4 inches \times 0.020—0.025 inch (thickness) in size. The 6 cathodes (made in accordance with the formulation described in Method 1) contained a total of 21 grams of manganese dioxide with 9 grams of conductive material and binder (2 per cent by weight polysulfone). The 7 anodes contained a total of 20 grams of zinc powder and 10 grams of starch-gelled 9 N KOH electrolyte pressed into tin-plated copper screen current collectors. An additional 20 grams of 9 N KOH were used in each cell. Separators of modacrylic fiber were employed adjacent to the cathodes and fibrous cellulose adjacent to the zinc anodes.

A suitable container weighs 20 grams; thus, the total unit cell weight is 100 grams (representing $1/9$ of a 9-cell, 12 volt battery). Unit cell capacity is a nominal 5 watt-hours, corresponding to approximately 25 Wh/lb at the 3-hour discharge rate (discharge to a cutoff of 0.9 volt in 3 hours).

Fig. 14 shows the 20-ampere discharge (the 6-minute rate) of such a cell arranged in 12 pulses, 5-seconds each, for 3 minutes, thereby taking $1/6$ of the total capacity out of the cell (at 20 amperes, a new cell operates for 6 minutes continuously until 0.9 volt is reached). After 20 charge-discharge cycles (in the 12th pulse of the 20th series), the cell reached 0.9 volt (see dashed curves in Fig. 14). This represents excellent performance considering that a commercial lead-acid cell of comparable size drops to 0.9 volt within one series of 20-A discharge pulses (20 ampere-minutes). It should be further noted that lead-acid batteries can tolerate high pulses in a daily sequence, but when put on shelf after such testing, their charge retention was extremely poor.

The variation in capacity of this cell at various discharge rates is shown below:

6-Hour Rate:	(0.7-A Discharge Current)	65
4 Ah	40—60 cycles	
3 Ah	80—100 cycles	
1.5 Ah	200 cycles	
3-Hour Rate:	(1.33-A Discharge Current)	70
4 Ah	60—80 cycles	
2 Ah	150 cycles	
1 Ah	300 cycles	
0.5 Ah	>800 cycles	
1-Hour Rate:	(4-A Discharge Current)	75
4 Ah	20—30 cycles	
6-Minute Rate:	(20-A Discharge Current)	80
2 Ah	12—15 cycles	
Example 8		
Manganese dioxide cathodes made according to this invention have demonstrated 90 per cent maintenance (charge retention) after 6 months storage at 45°C. in 9 N KOH.	85	
Alkaline manganese dioxide-zinc batteries (Fig. 16) made with the electrodes of this invention have also demonstrated a sizeable capacity advantage in early cycle life in continuous discharge in comparison with a commercial lead-acid battery of the same nominal voltage and design. On a 0.6-ohm constant resistance drain, the eight-cell alkaline manganese dioxide batteries operated for 4—6 minutes to the 0.9 V (per unit cell) cutoff, compared to the 45 seconds to 1 minute time-to-cutoff, advertised by the manufacturers of a 12-volt comparable sized lead-acid battery. The alkaline unit cells were constructed as shown in Fig. 15. There were 8 compartments in the battery (Fig. 16), each measuring 3.3 × 2.2 × 0.413 inches. Each unit cell contained 6 thin manganese dioxide cathodes and 5 zinc anodes (of #5/0 expanded zinc grids). The cathodes (each 0.02 inch thick) were made of the following formulation:	90	
	100	
	105	

Components	Wt. % of Finished Electrodes	110
35.8 g Electrolytic manganese dioxide	82	
3.6 g Powdered graphite	8.2	
0.72 g fibers (modacrylic or graphite)	1.6	115
1.8 g polystyrene	4.1	
1.8 g colloidal graphite	4.1	

The solvent used for the polystyrene was tetrahydrofuran. The cathode collectors were silver-plated steel; anode collectors were tin-plated steel. The electrolyte was 9 N aqueous

5 KOH containing 1% by weight ZnO. "Permion" separators (made by Radiation Application, Inc., Long Island City, New York) were used. "Permion" separators are commercial membranes composed of radiation grafted cellulose. The radiation grafted monomer is a material such as a methacrylate.

10 Fig. 17 illustrates the unit cell (Fig. 15) voltage on 0.6-ohm continuous drain on the 8-cell battery compared to that of a unit cell in the 6-cell commercial lead-acid battery. The manganese dioxide-Zn unit cell of this invention had a somewhat lower voltage but ran for a much longer time than the lead-acid cell at this drain. As many as 20 cycles under these discharge conditions were obtained from alkaline manganese dioxide cells of this size compared to only a few 15 cycles (e.g., 5) experienced with the lead-acid cell under the same conditions.

20 Unit alkaline manganese dioxide-Zn cells (Fig. 15) were also tested by pulsing under a 25 ampere pulse for 0.50 second once each minute. The discharge performance of several typical cells can be seen in Fig. 18, which shows that up to 4 recharges, 350 pulses were obtainable to a cutoff of 0.90 volt.

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30 Example 9

To illustrate the effect of liquid aqueous electrolyte on bonded electrodes, the following test was carried out. A number of disks containing 78 weight per cent manganese dioxide, 6 per cent Portland cement as binder, and 16 per cent powdered carbon was prepared. Other manganese dioxide disks containing 80 weight per cent manganese dioxide, 2 per cent polymethyl methacrylate binder, and 18 weight per cent particulate conductive material (both colloidal and non-colloidal) were made in accordance with a procedure analogous to Method 1. Samples of each type of disk were immersed in 9 N aqueous KOH at 50°C. for one week. At the end of this time, those disks bonded with Portland cement had already begun to crumble and exfoliate, whereas the polymer-bonded disks made according to this invention showed no evidence of disintegration.

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50 WHAT WE CLAIM IS:—

1. A coherent electrode for an electrochemical device having an aqueous electrolyte, which electrode is composed of (a) particulate manganese dioxide, (b) colloidal electrically conductive material, and (c) particulate electrically conductive material, said materials (a), (b) and (c) being bonded by an electrolyte-wettable polymeric binder, and said colloidal electrically conductive material providing particle-to-particle electrical contact within the electrode, the electrode being resistant to swelling an aqueous electrolyte.

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2. An electrode as claimed in Claim 1, in which said polymeric binder is an acrylonitrile-butadiene-styrene polymer, an epoxy resin, a polymerized lower alkyl ester of acrylic or methacrylic acid, melamine-formaldehyde resin, urea-formaldehyde resin, chlorinated polyether, polycarbonate, phenol-formaldehyde resin, polysulfone, polystyrene, styrene-acrylonitrile copolymer, polyvinyl chloride, vinyl chloride-vinyl acetate copolymer, polyvinyl alcohol, or styrene-butadiene copolymer.

3. An electrode as claimed in Claim 1, in which the polymeric binder is an epoxy resin, a polymerized lower alkyl ester of acrylic or methacrylic acid, polysulfone and polystyrene.

4. An electrode as claimed in any preceding claim in which colloidal electrically conductive material is graphite, carbon, or a powdered metal, and wherein the particulate electrically conductive material is graphite or carbon.

5. An electrode as claimed in Claim 4, in which the colloidal electrically conductive material is graphite.

6. An electrode as claimed in any foregoing claim in which the particulate electrically conductive material is acetylene black or powdered graphite.

7. An electrode as claimed in any preceding claim, which contains at least 1 weight per cent of said colloidal electrically conductive material, at least 5 weight per cent of said particulate electrically conductive material, at least 1 weight per cent of said polymeric binder, and at least 70 weight per cent of manganese dioxide, the percentages being based on weight of electrode.

8. An electrode as claimed in Claim 7, which contains from 1 to 2% by weight of colloidal electrically conductive material.

9. An electrode as claimed in Claim 7 or 8, which contains from 5 to 10% by weight of particulate electrically conductive material.

10. An electrode as claimed in Claim 7, 8 or 9, which contains from 1 to 2% by weight of polymeric binder.

11. An electrode as claimed in any preceding claim which has a thickness of from about 10 to about 50 mils.

12. An electrode as claimed in any preceding claim which is capable of utilizing at least 25 per cent of the electrochemical energy of the manganese dioxide contained in said electrode at a constant discharge current of 100 milliamperes per gram of manganese dioxide in said electrode versus a zinc reference electrode using 9 normal aqueous potassium hydroxide as the electrolyte, before the voltage drops under 0.9 volt.

13. An electrode as claimed in Claim 12, which is capable of utilizing at least 35 per cent of the electrochemical energy of the manganese dioxide contained therein.

14. An electrode as claimed in any of Claims 1 to 11, which is capable of utilizing at least 15 per cent of the electrochemical energy of the manganese dioxide contained in said electrode at a constant discharge current of 250 milliamperes per gram of manganese dioxide in said electrode versus a zinc reference electrode using 9 normal aqueous potassium hydroxide as the electrolyte before 10 the voltage drops under 0.9 volt.

15. An electrode as claimed in any preceding claim, which is capable of undergoing at least 150 charge/discharge cycles when discharged to 30 per cent of full discharge at a constant discharge current of 100 milliamperes per gram of manganese dioxide in said electrode.

16. An electrode as claimed in Claim 1 substantially as hereinbefore described with 20 reference to and as illustrated in the accompanying drawings and/or the foregoing examples.

17. An electrochemical device having an anode, a cathode, and an aqueous electrolyte in contact with said anode and cathode, in which, in the charged condition said cathode is the electrode as claimed in any of the foregoing claims.

18. An electrochemical device as claimed 30 in Claim 12 in which the anode is zinc, cadmium, lead, aluminium, or magnesium.

19. An electrochemical device as claimed in Claim 18, in which the anode is zinc.

20. An electrochemical device as claimed 35 in Claim 18, in which the anode is zinc or cadmium, and the electrolyte is aqueous alkali.

21. An electrochemical device as claimed in Claim 18 in which the anode is lead 40 and the electrolyte is aqueous acid.

22. An electrochemical device as claimed in Claim 18 in which the anode is magnesium and the electrolyte is aqueous magnesium bromide.

45 23. An electrochemical device as claimed in Claim 17 substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings and/or the foregoing examples.

50 24. A process for producing a coherent electrode for use in an electrochemical cell having an aqueous electrolyte, said process comprising:

(a) mixing (i) a polymeric binder, (ii) a 55 colloidal electrically conductive material, (iii) particulate manganese dioxide, and (iv) particulate electrically conductive material, to produce a mixture; and

(b) forming said mixture into a coherent 60 electrode, in which the polymeric binder is of a nature such that said electrode is wettable by said electrolyte.

25. A process as claimed in Claim 24, which process comprises:

(a) mixing (i) a first mixture of polymeric binder and a colloidal electrically conductive material, (ii) a particulate electrically conductive material, and (iii) particulate manganese dioxide, to produce a second mixture, and 65

(b) forming said mixture into a coherent electrode.

26. A process as claimed in Claim 25 in which step (b) of forming said second mixture into a coherent electrode includes contacting said second mixture with a current collector. 70

27. A process as claimed in Claim 25 or 26 in which step (b) includes subjecting said second mixture to pressure. 75

28. A process as claimed in any of Claims 24 to 27, in which the polymeric binder is an acrylonitrile-butadiene-styrene polymer, epoxy resin, polymerized lower alkyl ester of acrylic or methacrylic acid, melamine-formaldehyde resin, urea-formaldehyde resin, chlorinated polyether, polycarbonate, phenol-formaldehyde resin, polysulfone, polystyrene, styrene-acrylonitrile copolymer, polyvinyl chloride, vinyl chloride-vinyl acetate copolymer, polyvinyl alcohol, or a styrene-butadiene copolymer. 80

29. A process as claimed in Claim 28, in which the polymeric binder is an epoxy resin, a polymerized lower alkyl ester of acrylic or methacrylic acid, a polysulfone or polystyrene. 85

30. A process as claimed in any of Claims 24 to 29, in which the colloidal electrically conductive material is graphite, carbon, or a powdered metal. 90

31. A process as claimed in any of Claims 24 to 30, in which particulate electrically conductive material is carbon or graphite. 95

32. A process as claimed in any of Claims 24 to 31, in which the polymeric binder is employed as a solution or dispersion in a volatile liquid. 105

33. A process as claimed in any of Claims 24 to 32, in which the colloidal electrically conductive material is employed as a colloidal dispersion in a liquid. 110

34. A process as claimed in Claims 32 or 33 in which said volatile liquid is organic. 115

35. A process as claimed in Claim 34, in which the volatile liquid is an alcohol, ketone, chlorinated hydrocarbon or tetrahydrofuran.

36. A process as claimed in any of Claims 32 to 34, in which said volatile liquid is volatilized to form pores in the product electrode. 120

37. A process as claimed in Claim 24 substantially as hereinbefore described with reference to any of the foregoing Examples.

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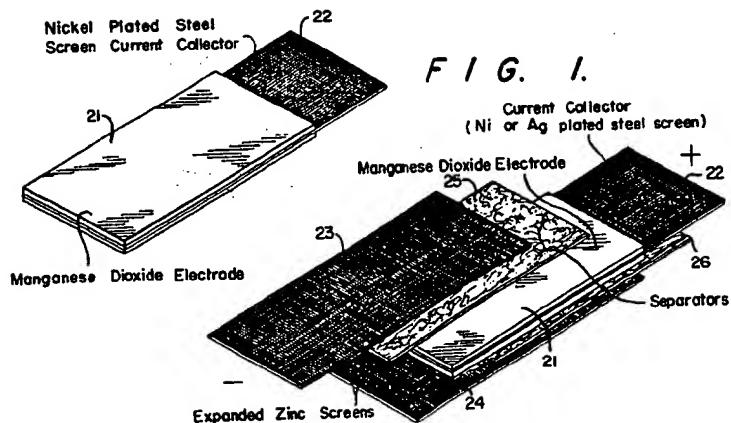
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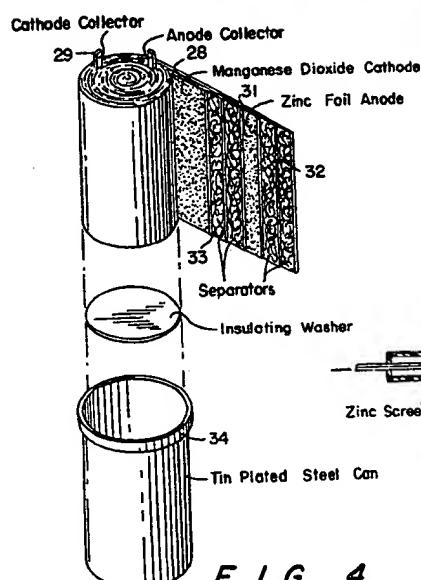
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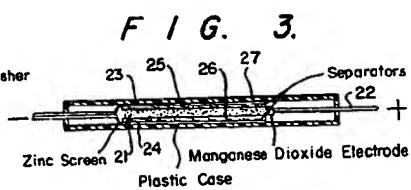
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F I G. 1.

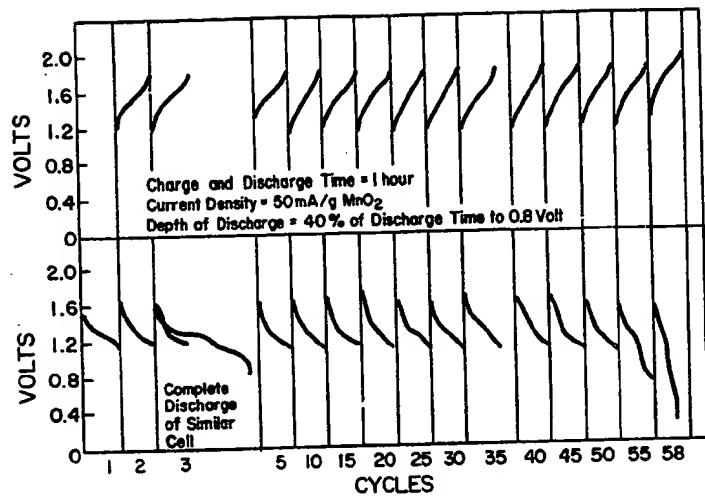


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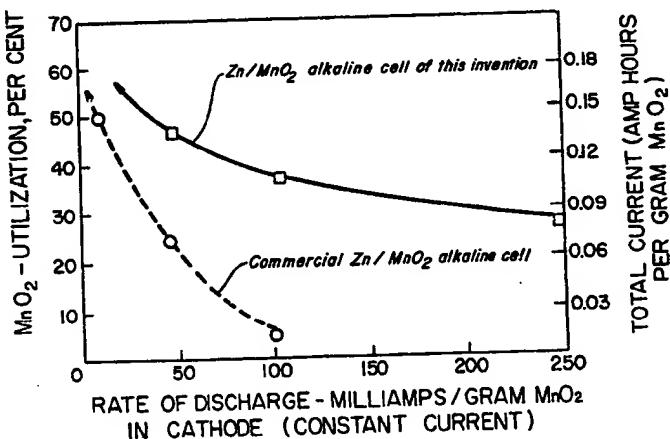


F I G. 3.

F I G. 4.



F I G. 9. CYCLING OF AN $\text{MnO}_2/\text{KOH}/\text{Zn}$ CELL



F I G. 5.

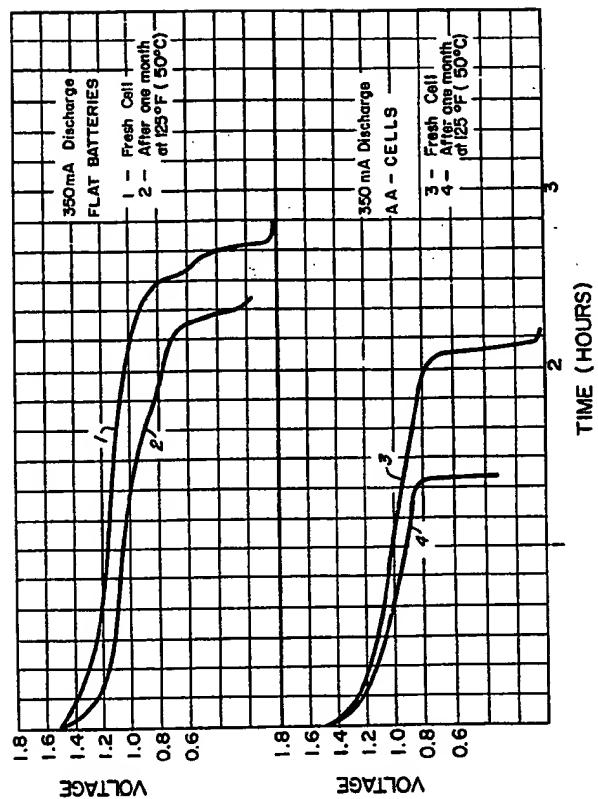


FIG. 6.

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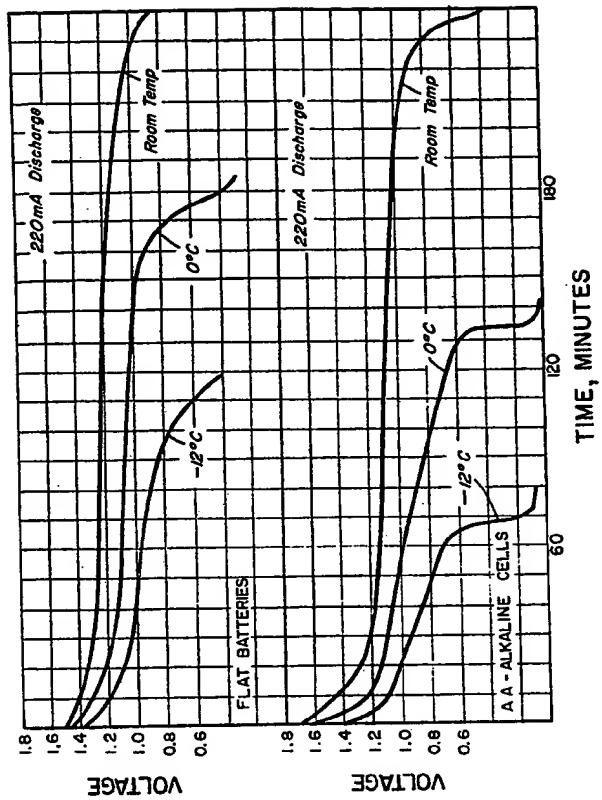
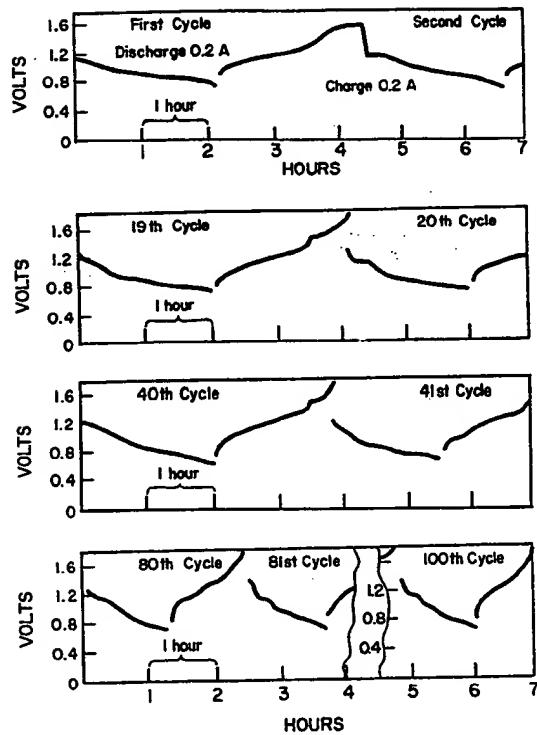


FIG. 7



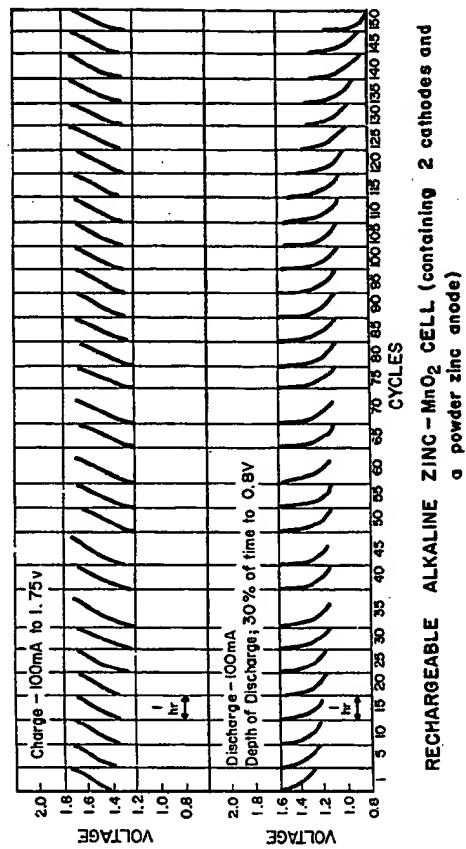
F I G. 8.

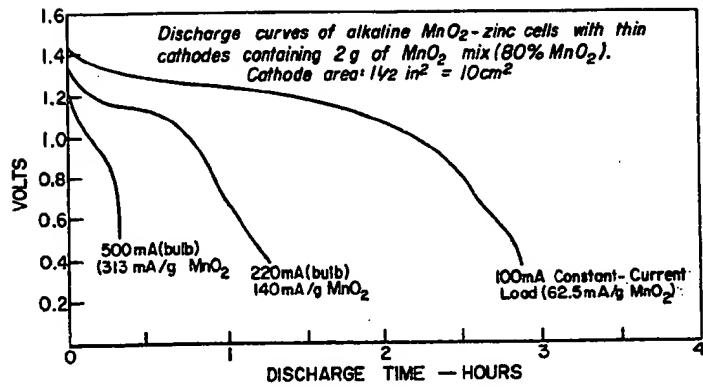
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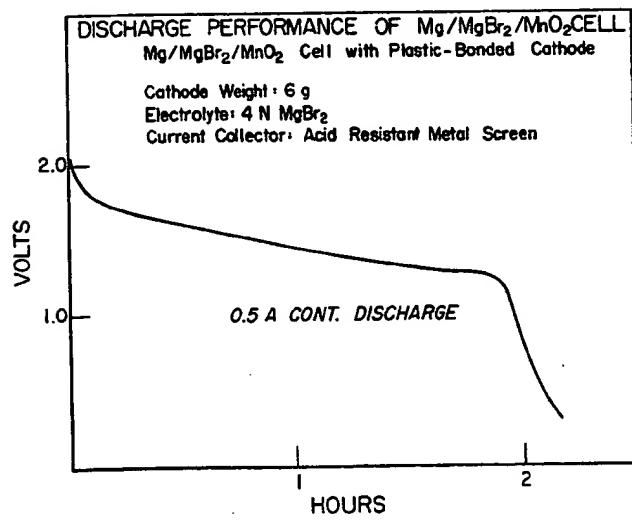
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F I G. 10.

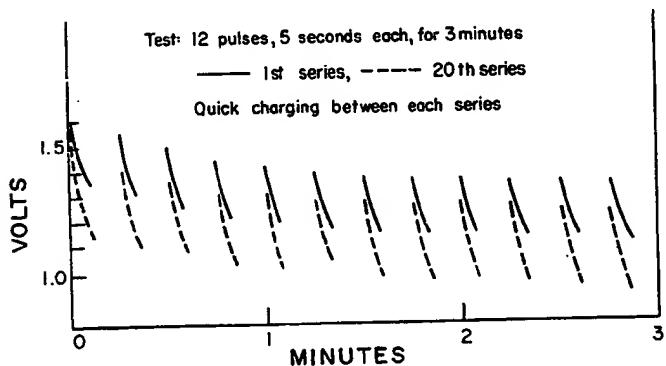
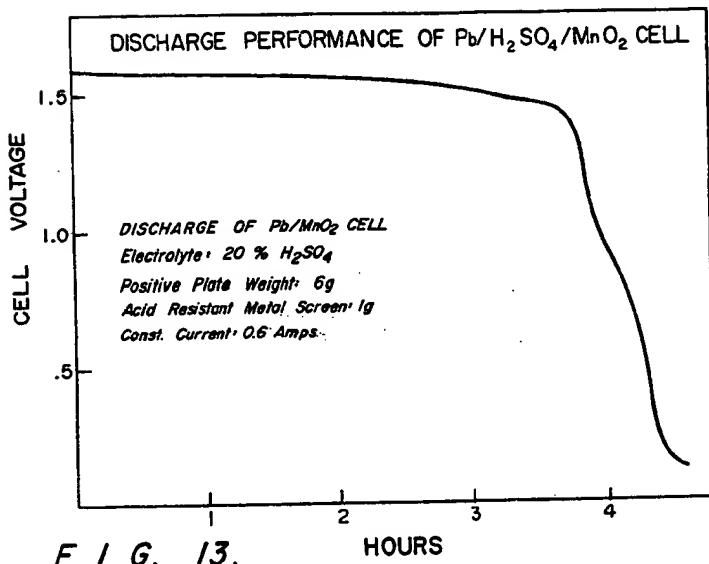




F / G. 11.



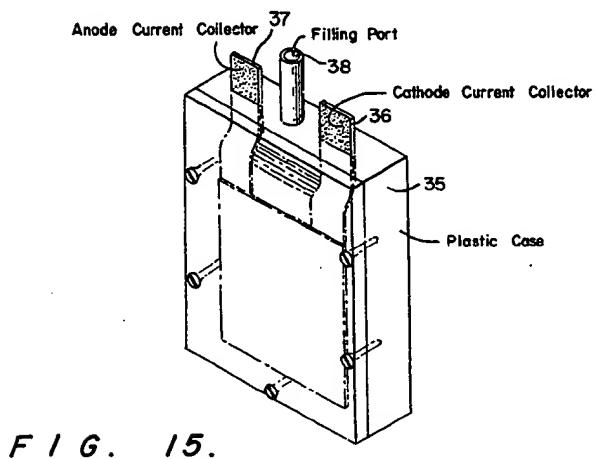
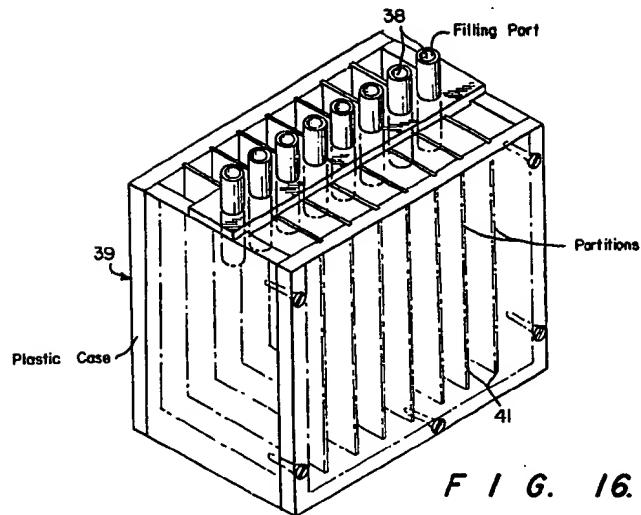
F / G. 12.

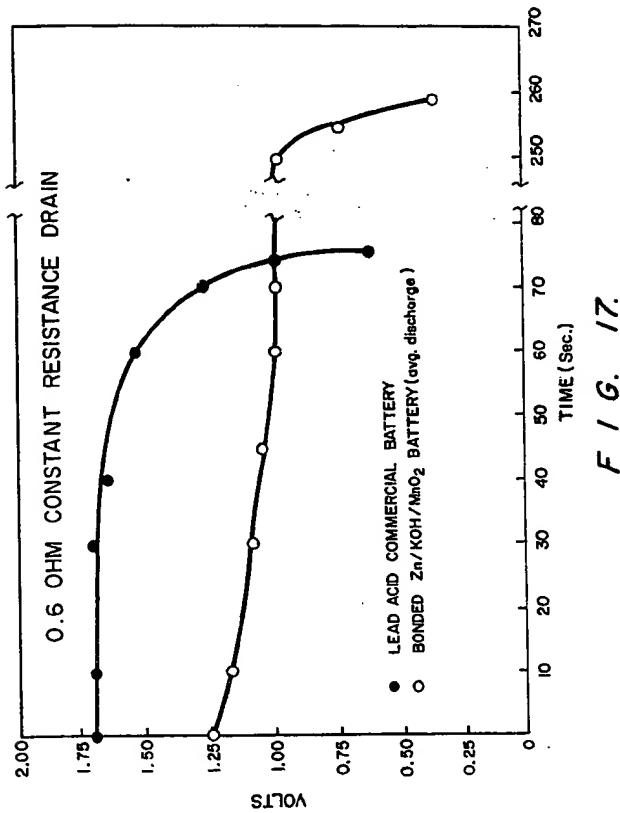


F / G. 14. 20 Ampere Pulsing of Cell of example 7
Recharging: 15 minutes at 1.7 Volt Constant
Voltage

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Sheet 9





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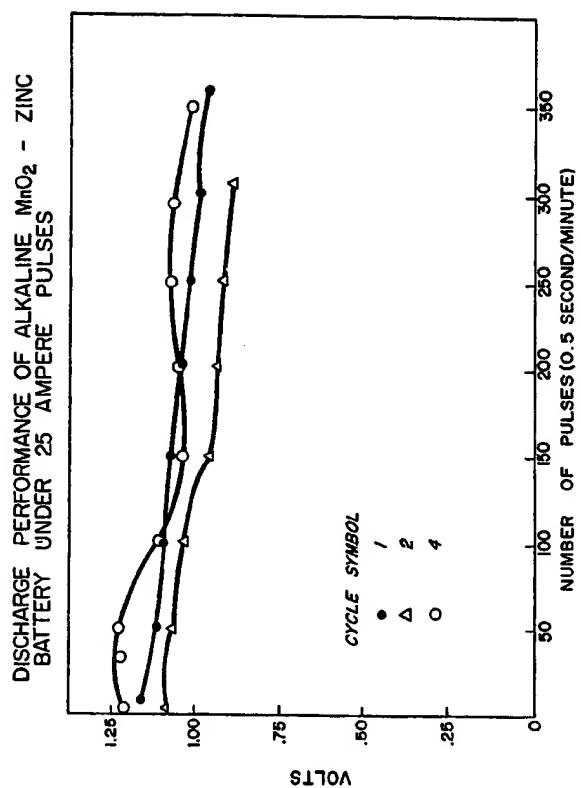
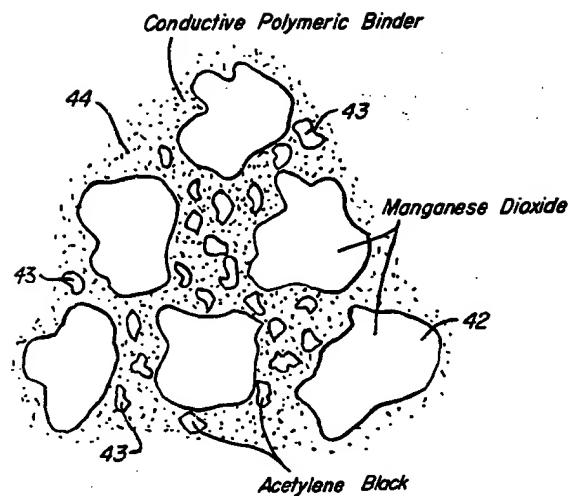


FIG. 18.



F I G. 19.